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**LOW TEMPERATURE PHOTOLUMINESCENCE  
CHARACTERIZATION OF ORBITALLY GROWN CdZnTe**

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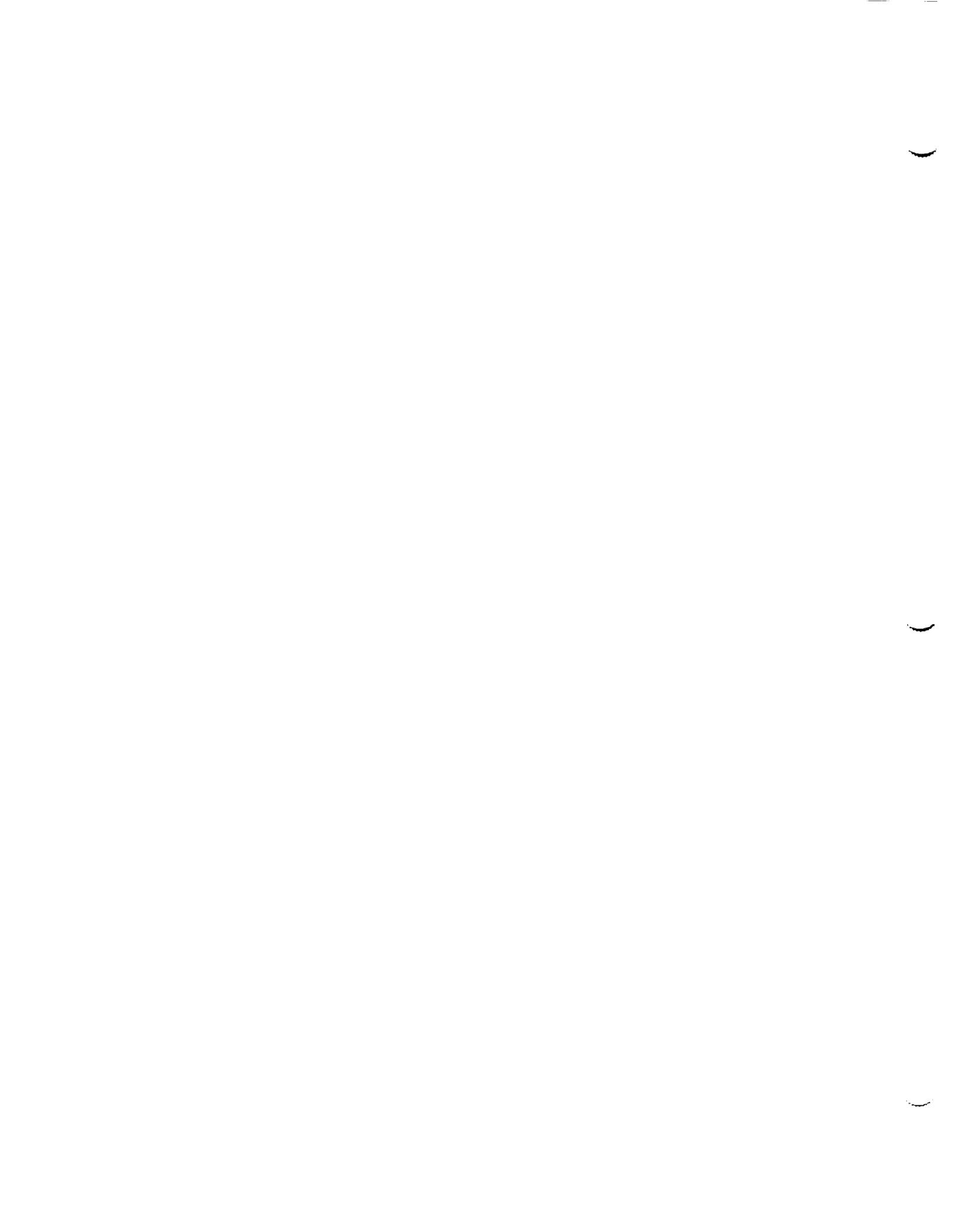
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## I. INTRODUCTION

The II-VI ternary alloy CdZnTe is a technologically important material because of its use as a lattice matched substrate for HgCdTe based devices. The increasingly stringent requirements on performance that must be met by such large area infrared detectors also necessitates a higher quality substrate.[Johnson, 1991; Magnea, 1987; Larson, 1993] Such substrate material is typically grown using the Bridgman technique. Due to the nature of bulk semiconductor growth, gravitationally dependent phenomena can adversely affect crystalline quality. The most direct way to alleviate this problem is by crystal growth in a reduced gravity environment. Since it requires hours, even days, to grow a high quality crystal, an orbiting space shuttle or space station provides a superb platform on which to conduct such research. For well over ten years NASA has been studying the effects of microgravity semiconductor crystal growth.[Curreri, 1996] This paper reports the results of photoluminescence characterization performed on an orbitally grown CdZnTe bulk crystal.

## II. EXPERIMENT

The bulk  $Cd_{1-x}Zn_xTe$  (nominal  $x = 0.04$ ) material was grown in the Crystal Growth Furnace (CGF) on board the space shuttle Columbia as part of the second United States Microgravity Laboratory (USML-2). The boule, prior to cleaving, was approximately 12 cm in length and 1.5 cm in diameter; see figure 1 for a schematic diagram. The boule was cut along 3 axes to yield wafers with different crystallographic orientations. Those with the prefix S are cross sections of the boule and cut longitudinally down its symmetry axis resulting in rectangular shaped wafers. The samples taken from the middle section of the crystal, OW1-OW13, were cut such that their surfaces are  $\{111\}$  planes. Because they were cut at an angle non-orthogonal to the growth axis the OW samples are oval in shape. The final group of samples were wafered from the "heel" end of the material and are designed W1-W6. The W samples were cut transverse to the growth direction, hence, they are round. The outer surface of the boule contained depressions dispersed around the circumference resulting from bubbles formed prior to solidification. During the cleaving process the cuts often intersected these depressions and appear as a semicircular notch on the circumference of the wafer. (These notches will be referred to as "scallops" throughout the rest of the paper.)

Excitation for the PL measurements was achieved with 5 mW of the 4880 Å line of an Ar<sup>+</sup> ion laser. The collected luminescence was focused onto the entrance slit of a SPEX double spectrometer and detected with a photomultiplier (PMT). The sample was cooled to 5 K in a

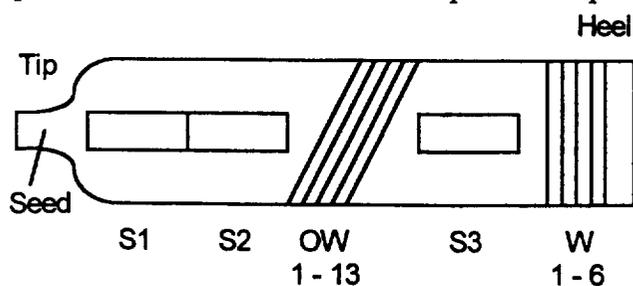


Fig. 1 Schematic diagram of the CdZnTe boule. S, OW, and W designate the three different wafer orientations.

continuous flow cryostat which was mounted on a mill-bed. The mill-bed provided translation in a plane perpendicular to the surface of the sample and parallel to the optics table. Motion in the third direction was provided by a micrometer mounted to the cryostat insert. The resolution of both positioning devices was at least an order of magnitude less than the smallest step size, 250  $\mu\text{m}$ , employed in the measurements.

### III. RESULTS AND DISCUSSION

A representative PL spectra, taken of wafer W4, is shown in figure 2. The dominant feature observed is the acceptor-bound exciton ( $A^{\circ},X$ ) peak at 1.610 eV. This peak is well resolved having a full width at half maximum (FWHM) of 2 meV. Moving up in energy from the  $A^{\circ},X$  a much less intense donor-bound exciton peak is located at 1.614 eV. The origin of these impurities is not certain but typical residual impurities often observed in this material system include Cu, Ag, Na, N, Ca, and Li. [Stadler, 1995] Although it is weak in intensity, the free-exciton peak (1.618 eV) is clearly present

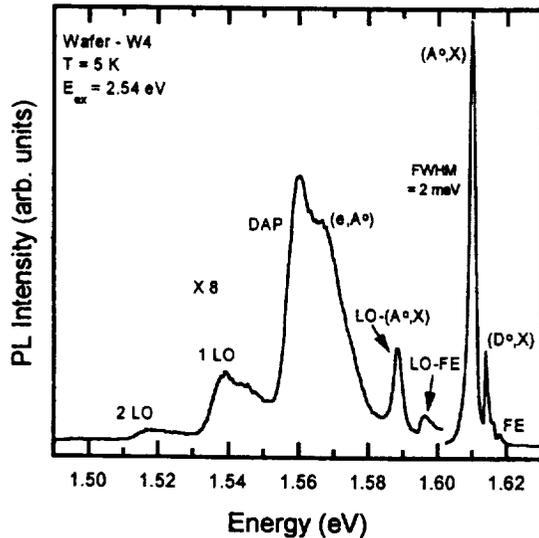


Fig. 2 Typical PL spectra showing all observed features.

Three orders of phonon replicas of the DAP and  $e,A^{\circ}$  are also distinct. In the energy region below 1.5 eV, where broad bands indicative of defects have been observed for this material system,[Stadler, 1995; Johnson, 1991] the spectra of the CdZnTe measured in this study did not exhibit any PL features. The absence of a broad defect band, coupled with the presence of several orders of phonon replicas and the narrow width of the  $A^{\circ},X$  peak, indicate that this material is of high quality.

In order to determine the Zn concentration of the material from the PL spectra the energy position of the free exciton peak, along with its known binding energy (10.4 meV)[Magnea, 1987] was utilized. The position of the free exciton peak, rather than  $A^{\circ},X$ , was chosen because: i) it was clearly observed in virtually all of the recorded spectra and ii) the acceptor bound peak, while much more intense, can vary in its energy position depending on the species of the dopant atom.[Tobin, 1995] The addition of the binding energy term to the exciton energy position yields an experimental energy bandgap. The Zn concentration is then determined from a comparison of this measured energy gap value with a known expression for the bandgap of  $Cd_{1-x}Zn_xTe$  as a function of  $x$ . A survey of the literature on CdZnTe revealed that there are many different, though similar, equations which express the relationship between the direct bandgap and the Zn concentration.[Tobin, 1995; Magnea, 1987; Stadler, 1995; Kennedy, 1988; Doty., 1992;

The region below  $A^{\circ},X$  in energy exhibits several features. The 1-LO phonon replicas ( $h\nu_{LO} = 21$  meV [Magnea, 1987]) of both the free-exciton and  $A^{\circ},X$  are distinct at 1.597 eV and 1.589 eV, respectively. In the energy region 1.565 eV it is clear that two peaks are overlapping. In order to determine their origin the excitation energy and temperature dependencies of this broad feature were investigated. The excitation study measured the energy position of the 1.565 eV bands over the incident power range 5 mW - 355 mW. The temperature study was conducted over the span 4.5 K - 120 K. From these two techniques it was determined that the lower energy peak (1.560 eV) is due to donor-to-acceptor (DAP) recombination and the 1.566 eV feature is band-to-acceptor ( $e,A^{\circ}$ ) emission.

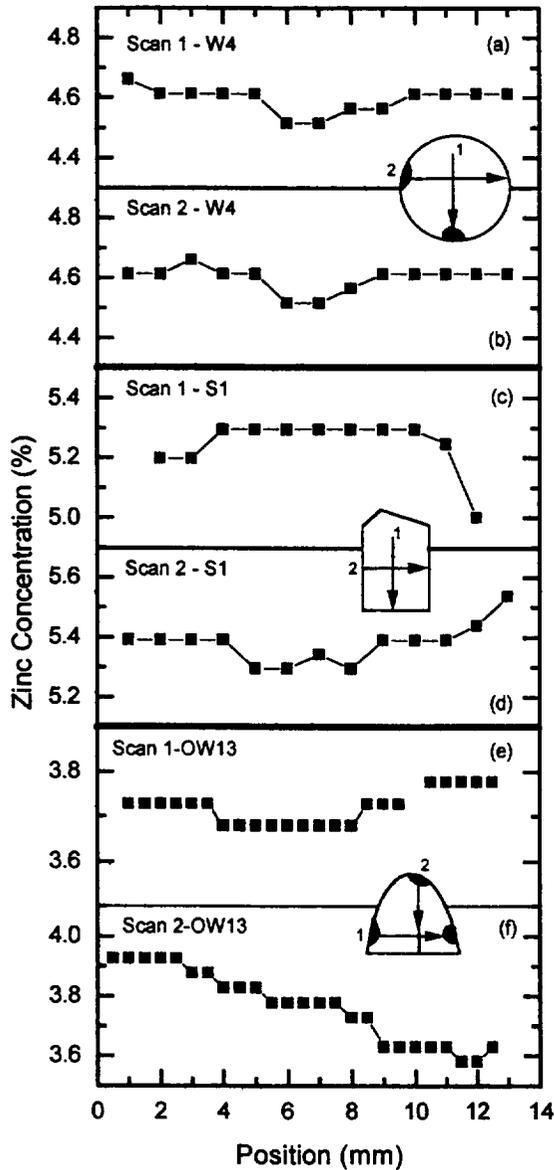


Fig. 3 Transverse Zn concentration across several different wafers. Position coordinate refers to distance from starting point of scan. Inset diagrams are of the wafer showing each scan. Black spots on edges represent the scallops.

region. The second scan performed on W4 began at the edge of a scallop and moved approximately along a diameter of the round sample terminating on the opposite edge. An analogous dip in the Zn fraction is apparent for scan 2, displayed in figure 3 (b). This change in concentration measured by scan 2 occurs in the same center region as observed in scan 1, i.e. the center portion of the wafer. Recall that the center of this wafer corresponds to the longitudinal axis of the original boule. The change in concentration, from the edge of the wafer to the center region, is  $\sim 0.1\%$ , greater than the point-to-point precision of the measurements stated above.

Pessa, 1993] In the current work the results of Magnea, al.[Magnea, 1987] and Doty, et. al.[Doty, 1992] were each applied and then averaged to obtain the final concentration value for each data point. The expressions of Magnea and Doty for the bandgap energy of  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  are

$$E_g(x) = 1.605 + 0.505x + 0.285x^2 \text{ (eV)} \quad (1)$$

and

$$E_g(x) = 1.6068 + 0.455x + 0.33x^2, \text{ (eV)} \quad (2)$$

respectively. The accuracy of this technique for determining the *absolute* Zn mole fraction is limited to  $\sim \pm 0.002$ , limited by the composition calibration.[Tobin, 1995] On the other hand, the estimated precision of the PL data is  $< \pm 0.001$  in concentration  $x$ .

Figure 3 shows the Zn concentration as a function of position for three separate wafers, one from each of the three regions of the boule (S, OW, and W) described in the previous section. The position coordinate is the distance from the starting position on the individual wafer for that particular scan. A schematic diagram of each of the 3 wafers has been included to indicate the orientation and direction of the two scans.

The results of the measurements on wafer W4 are shown in Figs. 3 (a) and (b). Scan 1 (fig. 3 (a)) begins 1-2 mm in from the edge of the sample and moves towards one of the scallops along the opposite edge. The last spectra in this scan was taken at the edge of the scallop on the polished surface. Immediately apparent from this data is the decrease in concentration for a 5 mm long portion of the wafer located in its center

Figures 3 (c) and (d) display the concentration dependence results for wafer S1. The first scan of this wafer began 4-5 mm in from one side and ended at an edge as shown in the diagram. This path is down the middle of the wafer which coincides with the center region of the boule (see figure 1). For this scan the concentration is seen to remain constant for most of the data, decreasing only at either end. The measurements which comprise scan 2 (fig. 3 (d)) were taken along a path that is approximately a diameter of the original boule. As seen for W4, scan 2 of S1 reveals that the concentration at the outer edges of the wafer is  $\sim 0.1\%$  higher than in a 5 mm region located near the center axis.

The concentration variation across sample OW13 is shown in figures 3 (e) and (f). Since this wafer is one from the OW group it is oval shaped. But, the wafer was broken and only one portion of this wafer was measured (see schematic diagram inset). The first scan, which ran in a transverse direction across OW13, began at the edge of a scallop on one side of the wafer and ended on the perimeter of another scallop located at the opposite side. The data (fig. 3 (e)) clearly shows, once again, a region of depressed ( $\sim 0.1\%$ ) concentration around the region of the longitudinal axis of the boule. The concentration dependence measured in scan 2, shown in figure 3 (f), exhibits a continuous decrease along the entire measured region. This occurs because scan 2 terminates at the broken edge of OW13, a point which would be located at the *center* region of the wafer were it whole.

The results from the three samples discussed above (W4, S1, and OW13) are indicative of those observed from all wafers measured in this work. There is an increase in Zn mole fraction when traversing a radius from the center of the cut wafers to their outer perimeter. This includes radii which terminate at one of the scallop shaped defects. There was no apparent anomalous fluctuation in the homogeneity of the CdZnTe in the region of these scallop features in comparison with a non-scallop wafer edge.

A plot of the longitudinal Zn fraction variation along the length of the original boule can be obtained by "reconstructing" the sample from the individual wafer measurements. A single concentration value for each wafer was determined by averaging the results obtained from the center portion of that wafer, i.e. the region in which the  $\sim 0.1\%$  concentration decrease was observed. The result of placing these concentration values in the correct sequential order is shown in figure 4. (It must be noted that the horizontal axis is only a list of the wafers and does *not* represent the actual spacing between the wafers.) From the center region of the plot it is apparent that the concentration fluctuation amongst the OW slices is reasonably small at only 0.7%. Wafers OW2 - OW5 exhibit a progressive decrease in Zn but are within 0.2% of one

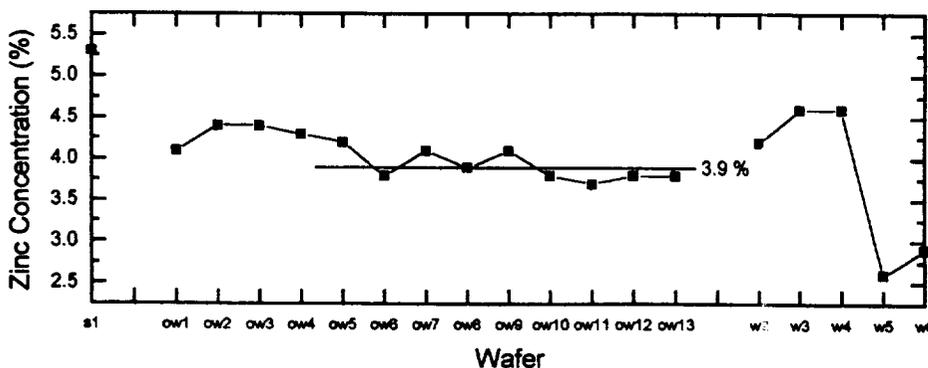


Fig. 4 Zn concentration variation along the boule axis. Solid line is at Zn = 3.9%, the concentration average of the last 8 OW wafers. Horizontal axis is not an accurate spatial depiction of boule length.

another. The individual Zn concentration of each of the last eight wafers in this set is within the experimental error of their average, 3.9 % (solid line in figure). Hence, the region between and including wafers OW6 and OW13 is, within the errors of these measurements, homogeneous. This is not the case for either end of the original boule. The data clearly shows that the “tip” portion of the boule (S1) has the highest ZnTe concentration at 5.3 %. At the “heel” end of the boule the Zn fraction rapidly increases (W2-W4) in comparison to the OW section and then drastically decreases to ~ 2.7 % for the last two wafers measured. These extremes are expected because of the radical growth conditions, e.g. quenching, experienced by the heel section.

#### IV. CONCLUSIONS

We have reported the results of PL characterization of twenty wafers cut from an orbitally processed CdZnTe sample. The sharpness of the near-band-edge features and the lack of any broad defect related bands is indicative of high quality material. The PL spectra also provided an accurate ( $\pm 0.2$  %) method to determine an absolute spatial variation of the Zn concentration. The PL technique also provides an even more accurate measurement ( $< \pm 0.1$  %) of the point-to-point concentration variation within a single wafer. It was found that there is an ~ 0.1 % increase in the ZnTe concentration along the radial direction moving from the central region towards the outer circumference of the boule. This region at the core of the sample is ~ 5 mm in diameter and runs the length of the boule. There was no noticeable difference in concentration, along the outer edge of the boule in the region of the “scallops” which are present in this particular sample. Longitudinally, the Zn fraction decreased from a high of 5.3 % in the “tip” to 2.6 % in the “heel” region. Through the middle region of the boule (OW section), the concentration remains relatively constant at ~ 3.9 %, in good agreement with the nominal concentration of 4.0 %.

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